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Optical Absorption in Two-Dimensional Random Lattices with Correlated Impurities

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We study optical absorption due to Frenkel excitons in two-dimensional systems with random distribution of impurities. We compare the absorption spectra of random lattices with correlated and uncorrelated disorder. We find that correlated disorder causes the occurrence of well-defined characteristic lines which clearly differ from the case of uncorrelated disorder. We are able to identify the origin of the absorption lines by considering the exciton dynamics in small clusters of sites forming the lattice.

1. Introduction

Optical properties of randomly disordered systems are a subject of long-lasting interest both from fundamental and applied viewpoints [1,2]. In the recent few years, we have carried out a great deal of work on coherent and incoherent exciton dynamics in one-dimensional (1D) systems with *correlated disorder* and we have found that correlations have profound effects on their physical properties [3 to 6]. The notion of correlated disorder implies that certain physical parameters in random systems are not completely independent within a given correlation length, thus leading to a competition between short-range order and the underlying long-range disorder. The occurrence of correlations in some polymers like polyaniline was previously pointed out by Dunlap et al. in [7], so that we believe that the interest of these works is beyond the formal study of exciton dynamics. Correlations in 1D disordered systems are revealed in the absorption spectra of Frenkel excitons through well-defined characteristic lines not shared by uncorrelated ones [4]. The so-called *two-center* model, which describes the absorption spectrum of two isolated and coupled sites, leads to analytical expressions which successfully explain the absorption spectra of the whole system [4]. Therefore, the presence of correlations in random systems can be readily determined from the analysis of the optical absorption spectra of these samples.

In this paper we extend our previous results to two-dimensional (2D) random systems with correlated and uncorrelated disorder. This task involves the generalization of the above-mentioned two-center model since, as it will be discussed later, it does not suffice to understand the origin of all lines observed in the absorption spectra of 2D Frenkel systems. The obvious way to proceed is to consider small clusters with larger number of sites (hereafter referred to as M-center model, with $M \geq 2$). Then, the number of possible optical transitions increases dramatically and a careful analysis is required in order to ascertain the origin of the absorption lines of 2D Frenkel systems. Recently, Nebatani et al. [8] have demonstrated the 2D nature of the excitons in a monolayer of a cyanine dye and performed numerical simulations to compare their results with optical spectra obtained experimentally [9]. Our results would help to understand exciton dynamics in actual 2D systems and to explain the origin of the features observed in the optical absorption spectra.

2. Model

The Hamiltonian of the Frenkel-exciton problem for a system of $\mathcal{N} = N \times N$ centers with nearest-neighbour interactions can be written in the tight-binding form

$$\mathcal{H} = \sum_{k} V_k a_k^\dagger a_k + \sum_{(k,l)} T_{kl} (a_k^\dagger a_l + a_l^\dagger a_k) \,. \tag{1}$$

Here a_k and $a_k^\dagger$ are the exciton annihilation and creation operators in the site representation, respectively. V_k is the transition frequency at site k ($\hbar = 1$). The sum (k,l) runs over pairs of nearest neighbours and T is the coupling constant, which is assumed to be the same over the whole lattice. In our model, transition frequencies can take on two values, namely V (host sites) and V' (impurities), the last one being randomly distributed across the lattice in two different ways, uncorrelated or forming pairs of neighbouring sites (which will be referred to as *dimer* defects).

The coupling T_{kl} is due to the dipole–dipole interaction between sites whose positions are $\mathbf{r}_k$ and $\mathbf{r}_l$. Let $\mathbf{d}_k$ be the transition dipole moment at site k and $\mathbf{r}_{kl} \equiv \mathbf{r}_k - \mathbf{r}_l$. Thus, the coupling is given as

$$T_{kl} = \frac{1}{r_{kl}^5} \left[r_{kl}^2 \mathbf{d}_k \cdot \mathbf{d}_l - 3 (\mathbf{d}_k \cdot \mathbf{r}_{kl}) (\mathbf{d}_l \cdot \mathbf{r}_{kl}) \right] . \tag{2}$$

For simplicity we assume that the dipoles are equal and perpendicular to the plane of the 2D regular lattice so that $T_{kl} = r_{kl}^{-3} \mathbf{d}_k \cdot \mathbf{d}_l \equiv T > 0$. Notice that r_{kl} is nothing but the lattice spacing whenever sites k and l are nearest neighbours.

The absorption line shape $\varrho(E)$ of an optical absorption process in which a single exciton is created in a system with $\mathcal{N}$ is given by (see [10])

$$\varrho(E) = -\frac{2}{\pi \mathcal{N}} \int_0^\infty \mathrm{d}t \, \mathrm{e}^{-\alpha t} \sin(Et) \, \mathrm{Im} \left(\sum_k G_k(t) \right) , \tag{3}$$

where the factor $\exp(-\alpha t)$ takes into account the broadening due to the instrumental resolution function of half-width α, and the Green functions $G_k(t)$ obey the equation of motion

$$i \frac{\mathrm{d}}{\mathrm{d}t} G_k(t) = \sum_l H_{kl} G_l(t) \,, \qquad t > 0 \,, \tag{4}$$

with the initial conditions $G_k(0) = 1$ and free boundaries are assumed. Here H_{kl} denotes the Hamiltonian elements in the site representation.

3. Results and Discussions

We have solved the equation of motion (4) for 2D systems with $\mathcal{N} = 100 \times 100$ sites using an implicit (Crank-Nicholson) integration scheme [11]. Once the functions $G_k(t)$

are known, the line shape $\varrho(E)$ is evaluated by means of (3). Energy will be measured in units of T whereas time will be expressed in units of T^{-1}. We have set $V = 5$, $V' = 15$ and $T = 1$. The width of the instrumental resolution is $\alpha = 0.15$; larger values of α result on spectra in which some of the lines are hidden. As a rule, we take α less than the minimum distance between two consecutive lines. The maximum integration time and the integration time step were 50 and 1.25×10^{-2}, respectively; larger maximum integration times or smaller time steps led to the same general results. The impurity concentration c ranged from 0 up to 0.40. We have averaged the results over 15 realizations of random distributions of impurities.

In the absence of impurities the spectrum is a single Lorentzian line centered at $E = V + 4T = 9$, as seen in Figs. 1 and 3 for $c = 0$. When impurities are introduced in the lattice, a broadening of this main line is observed accompanied by a shift of its position to lower energies on increasing impurity concentration. Keeping this result in mind, we now proceed to discuss the main features of the spectra obtained when impurities are present in the system.

3.1 Uncorrelated impurities

Fig. 1 shows the different lines observed in the absorption spectra for varying c. First of all, we observe the above-mentioned redshift and broadening of the main line with increasing c. The displacement of this line is linear for small concentration of impurities ($c \leq 0.10$) but quadratic for larger values of c, as it can be observed from Fig. 2. Besides, four satellite lines occur at energies $E_1 = 15.40$, $E_2 = 16.26$, $E_3 = 16.66$, and $E_4 = 16.94$, which appear for concentrations above the values $c = 0.02$, $c = 0.02$, $c = 0.10$,

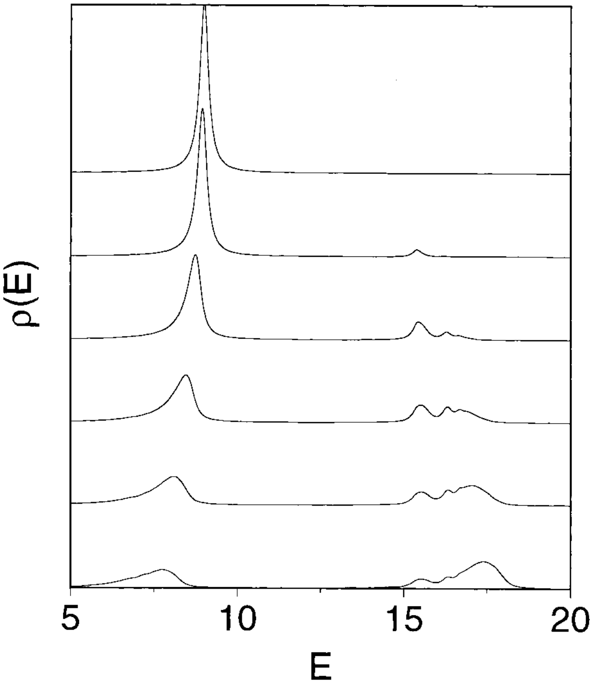

Fig. 1. Absorption spectrum for 100×100 lattices with different concentrations c of unpaired impurities. From top to bottom $c = 0$, 0.02, 0.10, 0.20, 0.30 and 0.40. All curves have equal area

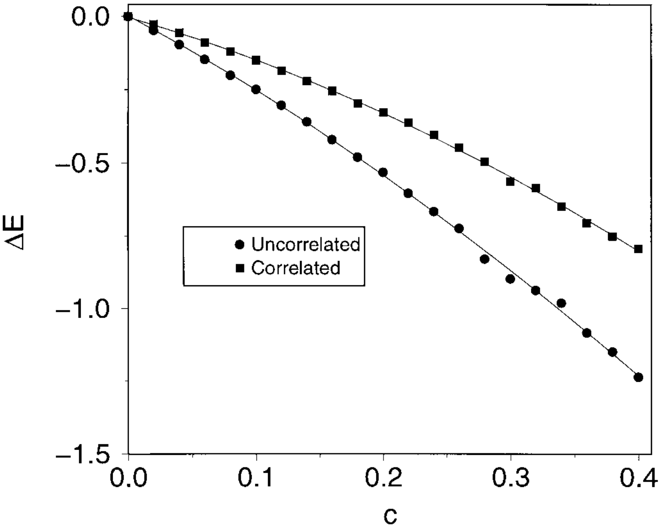

Fig. 2. Shift of the main absorption line for 100 × 100 lattices, defined as $\Delta E = E(c) - E(c=0)$, as a function of the concentration c of uncorrelated (circles) and correlated (squares) impurities. Solid lines show the least squares fit to quadratic functions

and $c = 0.26$, respectively. The intensity of the satellite lines increase at the expense of the decrease of the main absorption line. In addition, they slightly shift to higher energies with increasing c.

In order to study the results from a quantitative point of view, we consider the M-center problem, which describes the optical absorption spectrum of the cluster formed by M isolated and coupled centers. The equation of motion (4) can be easily solved whenever M is kept small (we have restricted ourselves to $M \leq 6$). In such a case, we only need to diagonalize the $M \times M$ matrix whose diagonal elements are the transition frequencies of the small cluster and the off-diagonal elements are equal to T. Therefore, the optical absorption spectrum of the isolated cluster with M centers presents M lines at most. The weight of each line in the absorption spectrum of the cluster is given by its oscillator strength which, in turn, is proportional to $\left(\sum_{j=1}^{M} a_j^{(n)}\right)^2$. Here $a_j^{(n)}$ is the j-th component of the n-th eigenvector. Notice that only those states with nonvanishing oscillator strength contribute to the absorption spectrum of the cluster. For brevity we

Table 1
Summary of the energy of the satellite lines observed in the spectra of 2D systems with uncorrelated impurities and their origin within the M-center approach

energy	cluster
$E_1 = 15.40$	VV′
$E_2 = 16.26$	V′V′
$E_3 = 16.66$	V′V′V′
$E_4 = 16.94$	V′V′V′V′

do not write down explicitly the solution and only quote the final result (the corresponding expressions for the case $M = 2$ can be found in [4]).

The satellite line centered at E_1 arises from pairs VV′ which, considered as isolated systems of two coupled centers, present an eigenenergy $E = 15.10$ with our chosen parameters. The satellite line at E_2 emerges from pairs V′V′ (dimers), which have an eigenenergy $E = 16.00$. The intensity of this line is less than that of the line at E_1 for low c because the number of V′V′ pairs is less than the number of VV′ pairs in this case. Nevertheless, with increasing c, the second line becomes more intense as the number V′V′ pairs present in the lattice turns out to be significant. As for the third line, it comes from linear clusters of the form V′V′V′, which have an eigenenergy $E = 16.41$. In the same way, the fourth line is due to clusters composed by four impurities V′V′V′V′, which occur in a significant number for larger c. Anyway, this last line tends to be broader than the rest so that it overlaps with other lines proceeding from other non linear blocks of impurities that we have not taken into account in our study. Table 1 presents a summary of the energy of the satellite lines observed in the spectra of 2D systems with uncorrelated impurities and the origin we suggest within the M-center approach.

3.2 Correlated impurities

Let us now turn our attention to the case of correlated impurities, when dimer defects are intentionally introduced in the random lattice (see Fig. 3). We observe again the redshift and broadening of the main line with increasing c when correlations are present in the system, as it is shown in Fig. 2. However, this shift is smaller than that

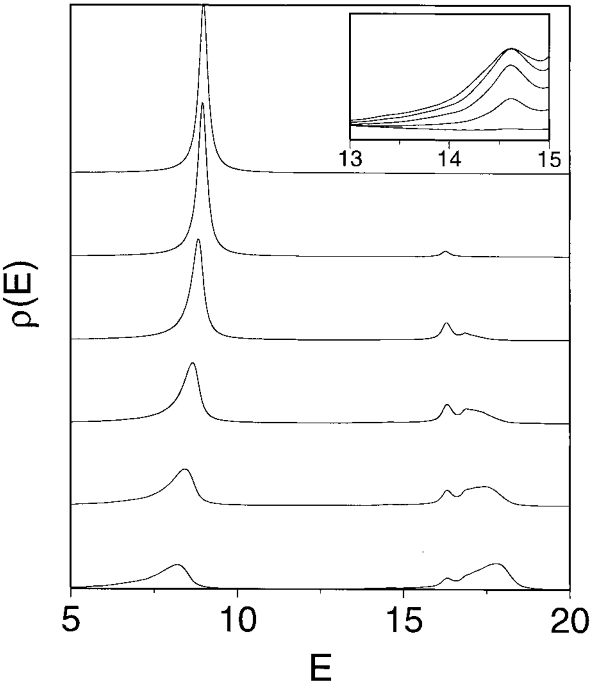

Fig. 3. Absorption spectrum for 100×100 lattices with different concentrations c of paired impurities. From top to bottom $c = 0$, 0.02, 0.10, 0.20, 0.30 and 0.40. All curves have equal area. The inset shows an enlarged view of the spectra for $c > 0$

Table 2

Summary of the energy of the satellite lines observed in the spectra of 2D systems with correlated impurities and their origin within the M-center approach

energy	cluster	
$E_1 = 16.26$	V′V′	
$E_2 = 16.84$	V′V′V′V′	(linear)
$E_3 = 14.62$	V′V′V′V′	(linear)
$E_4 = 17.14$	V′V′V′V′	(square)
$E_5 = 17.45$	V′V′V′V′V′V′	

observed in systems with the same concentration of uncorrelated impurities due to the fact that there exist larger areas without impurities. The satellite lines of the absorption spectrum are clearly different for equal values of c when disorder is correlated. Fig. 3 also shows five satellite lines at $E_1 = 16.26$, $E_2 = 16.84$, $E_3 = 14.62$ (see the inset of Fig. 3), $E_4 = 17.14$ and $E_5 = 17.45$ which appear for concentrations above the values $c = 0.02$, $c = 0.04$, $c = 0.04$, $c = 0.22$, and $c = 0.30$, respectively. These lines show the same evolution with c as in the uncorrelated case.

The line at E_1, which also appears in the case of unpaired impurities, is due to dimers V′V′. The coupling of two dimers to form a linear cluster V′V′V′V′ originates the line centered at E_2 (also observed in 2D systems with uncorrelated disorder) and the weaker line centered at E_3. This structure has the eigenenergies $E = 16.60$ and 14.38 with oscillator strength 0.95 and 0.05, respectively, in agreement with the ratio of intensities observed in our synthetic spectra. This agreement reinforces our suggestion regarding the origin of the lines. The lines at E_4 comes from the coupling of two dimers forming a 2×2 cluster, which has an eigenenergy $E = 17.00$. Finally, the line at E_5 is due to the coupling of three dimers to form a linear cluster V′V′V′V′V′V′, which has an eigenenergy $E = 16.80$. As in the uncorrelated case, this line overlaps with other lines coming from more complicated arrangements of impurities involving a higher number of centers. Table 2 presents a summary of the energy of the satellite lines observed in the spectra of 2D systems with correlated impurities and the origin we suggest within the M-center approach.

4. Conclusions

We have studied the absorption spectrum due to creation of Frenkel excitons in 2D random systems with correlated impurities, the correlation length being of the order of the lattice spacing. By comparing the obtained spectra with those corresponding to uncorrelated random impurities we are able to identify characteristic absorption lines which are directly related to the presence of correlated impurities. Furthermore, by considering small clusters of sites (M-center model), we have elucidated the origin of the different lines observed in the spectra.

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